

# 1992 Annual Report

## ***RESEARCH AND DEVELOPMENT***

Laboratory Services Branch  
Ontario Ministry of the Environment

May, 1993

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## Table of Contents

	<u>page</u>
<b>Overview</b>	1
<b>Air Resources Branch Support</b>	
I. Determination of Metals in Whatman 41 Filter Samples from Personal Monitors as Part of the Windsor '92 Study	2
II. Determination of Arsenic in APIOS Lo-Vol 28 Day Filter Packs	3
III. The Determination of Hexavalent Chromium in Air Particulates	5
IV. Evaluation of a Real Time PAH Monitor	6
<b>Water Resources Branch Support</b>	
I. PAH Storage Study	7
II. Disinfection By-Products	9
III. Micro-Extraction Methods for Drinking Water	10
IV. Automated Determination of Mercury at Ultra-Trace Concentrations in Waters by Gold Amalgam Preconcentration and Cold-Vapour Atomic Fluorescence Spectrometry	12
V. Detection of Sulphur Compounds by Ion Chromatography	13
VI. Mercury Determination by ICP-MS	14
VII. Improved Extraction Methods for PCDDs and PCDFs in Aqueous Samples	15
VIII. Analysis of Sewage Sludge for Organic, Extractable Priority Pollutants	16
<b>Multi-Program Support</b>	
I. Negative Ion Chemical Ionization (NICI) Confirmation of Halogenated Organic Compounds	18
II. LC-MS Analysis of Environmental Samples	20
III. Determination of As and Se in Environmental Samples by Flow-Injection Hydride Generation Atomic Absorption Spectrometry	21
IV. Extraction of Chlorophenols from Sediment by Supercritical Fluid Extraction	22
<b>Publications and Presentations - 1992</b>	24

## Overview

### Ray E. Clement, Chair, R&D Committee

Every aspect of environmental investigation must be supported by chemical analyses. Whether the purpose is to identify new pollutants, survey contaminated areas, track down the sources of pollution, support litigation activities, or any number of other activities, the Laboratory Services Branch is responsible for ensuring that other Branches of the Ministry of Environment and Energy are supplied with the analytical data needed to ensure success. Because the nature of environmental investigations is ever-changing, our clients often request services that we have not previously supplied. In fact, it is not unusual to receive a request to perform analytical work of a completely novel nature. In such cases, standard methods may be totally inadequate and we are required to perform development work to meet the needs of our clients.

This applied R&D work is an important, ongoing part of the service supplied by the Laboratory Services Branch (LSB). In addition to direct requests for new services from our clients, LSB staff also initiate studies designed to improve our existing methods to produce data of ever-increasing reliability. Improved detection limits, precision and accuracy, and improved ruggedness are frequently the principal goals of internally-directed development work, whereas increasing the range of application of our methods and lowering detection limits are the most frequent requests of our clients. In recent years, there has also been movement towards the "greening" of the laboratory - that is, to reduce the volume of organic solvents (some of them toxic), that are used in our analytical procedures. In addition to serving our clients better, these ongoing improvements in chemical analyses generally result in a net saving of time and money.

In this report are described the principal applied R&D studies that were conducted in 1992. The enhancements to our analytical capabilities that result from this work are important to allow LSB staff to most effectively support the many activities of the Ministry of Environment and Energy.

# Air Resources Branch Support

## Introduction

This year, most of our development work in support of Air Resources Branch programs was in the area of trace metal determinations. Improved methods for sampling and analysis of arsenic and hexavalent chromium in ambient air were developed. The use of personal samplers for trace metal determinations, and the rapid analysis of polycyclic aromatic hydrocarbons in air were also investigated.

## I. Determination of Metals in Whatman 41 Filter Samples from Personal Monitors as Part of the Windsor '92 Study

Study Leader: J. Hipfner

Study Team: R. Bell, M. Spencer, M. Powell

### *Introduction and Objectives*

Sampling by use of personal monitors can give direct evidence of human exposure to pollutants. However, analytical methods must be able to reach very low detection limits to detect pollutants from personal sampler monitors because sample sizes are very low. In this investigation, the methodology for sample extraction and sub-ppb determination of metals from Whatman 41 filters will be developed and validated. These methods will be applied to the determination of trace metals in personal exposure samples collected as part of the Windsor '92 study (Air Resources Branch).

### *Results*

Previously, these types of analyses were performed by using atomic absorption spectrometry (AAS) detection. To achieve the lower detection limits required for our Air Resources Branch studies, the more sensitive technique of Inductively-Coupled Plasma-Mass Spectrometry (ICP-MS) was employed. This permitted detection limits for most metals to be lowered by factors of about 5-10 times. The principal challenge in this work was blank control at these lower levels of detection. Ultra-high purity reagents were needed to control blank contamination, and many blanks and spike recovery samples were analyzed during the course of this work to provide a greater degree of quality control. Detection limits of metals on the order of  $0.1 \text{ ng/m}^3$  are possible by using the ICP-MS based method, compared to average detection limits of  $1 \text{ ng/m}^3$  or greater with the older AAS based method.

### *Work to be Completed*

The study is complete, and the new method is being used to determine metals in real-matrix samples. The detailed bench method documentation is being prepared.

## **II. Determination of Arsenic in APIOS Lo-Vol 28 Day Filter Packs**

Study leaders: J. Hipfner

Study Team: M. Shackleton, M. Powell, H.S. Chiu

### *Introduction and Objectives*

APIOS 28-day filter packs are not currently used for the determination of arsenic in air. As part of the MOEE Air Toxics program, an effective sampling and analysis method for As in air was required. Recoveries of arsenic by aqueous and acid extractions, and different filter pack configurations were investigated in this study.

### *Results*

Sampling was conducted to determine the optimum configuration of the filter packs for As and other metals in air. The following configurations were tested:

1. Whatman 40 filter/nylon filter/Whatman 41 - potassium carbonate
2. same as #1 with addition of polyethyleneimine filter
3. Whatman 40 filter/nylon filter/double polyethyleneimine filter
4. teflon filter/nylon filter/Whatman 41 (potassium carbonate)/polyethyleneimine

It was found that depending on the seasonal variation, 60-85% of the As could be found on the first Whatman filter. This showed that breakthrough of As from the filter pack used was not a problem, and that factors such as convenience and extraction efficiency were more important to the selection of the final filter pack configuration. By using a system that can be water-extracted, followed by ICP-MS analysis, detection limits for As in air of about  $0.1 \text{ ng/m}^3$  could be obtained. High purity acids are mandatory for this work, and there was no need for perchloric acid digestions for ICP-MS analysis.

### *Work to be Completed*

The principal objective of sampling air for As determination was achieved. Some additional work to investigate which filter configuration is most efficient and convenient is planned. It is possible that a double nylon filter by itself is sufficient for this application.

### III. The Determination of Hexavalent Chromium in Air Particulates

Study Leader: J. Hipfner

Study Team: R. Bell, M. Spencer, H.S. Chiu, D. Sturgis

#### *Introduction and Objectives*

Hexavalent chromium [Cr(VI)] is a suspected carcinogen. Concern over the concentrations of Cr(VI) in air have been raised as part of the "Cities of the 90's" study. A literature survey has shown that from 10% to 40% of total Cr in air is in the Cr(VI) form. The principal objective of this research is to establish a standard method for Cr(VI) in air based on ion chromatography separation and detection.

#### *Results*

The development work for this method has been completed. To simplify sample preparation for ion chromatography (IC), impingers that contain sodium carbonate/bicarbonate solution (used as eluent for IC) were employed. After preconcentration on an IC cartridge, the analyte was eluted and reacted with diphenyl carbazide to enable colorimetric detection of the chromium. Detection limits as low as 10 ppt using standards could be achieved, and recoveries from spiked impingers were in the range 85%-105%. The method as developed is specific for Cr<sup>6+</sup>.

#### *Work to be Completed*

A report of the method development, and full bench-method description, are in preparation.



#### **IV. Evaluation of a Real Time PAH Monitor**

Study Leader: P. Yang  
Study Team: N. Bouncore

##### *Introduction and Objectives*

By utilizing photoelectric excitation/emission processes for chemical analysis, it is possible to generate real-time data for polynuclear aromatic hydrocarbons (PAH) in air. While it can take more than eight days to generate analytical data for PAH concentrations by using conventional Hi-Vol sampling and GC/MS analysis, technology exists that can generate quantitative data of PAH (> 3-ring) in air within one minute - with detection limits in the ng/m<sup>3</sup> range. The objective of this study is to compare the data generated by a PAH real time monitor and by conventional sampling and analysis.

##### *Results*

An EcoChem Technologies PAS-1000i real-time PAH monitor was installed next to a Beta Gauge Particulate Analyzer (Anderson Instruments, Atlanta, Georgia) for particulate monitoring, and a Monitor Lab Model 8850 Fluorescent SO<sub>2</sub> Analyzer (Englewood, CO) for the determination of total reduced sulphur (TRS). Outputs from these three instruments were connected to a data logger and were pooled daily via the Ontario Air Quality Index Network's VAX 780 computer for data storage.

By using the real-time PAH and other data (TRS, particulate, wind direction), the West Central Region was able to correctly identify the specific sources of PAH emissions. To compare the results of the real-time monitor with those of conventional Hi-Vol and GC/MS methodology, only three simultaneous sampling events were available. However, the correlation between the real-time monitor and the much slower conventional method was excellent ( $r^2 = 0.9999$ ).

##### *Work to be Completed*

Additional validation work in cooperation with the manufacturer of the real-time PAH monitor and with regional staff is planned.

# Water Resources Branch Support

## Introduction

Our service to the Water Resources Branch improved in a number of areas from development work performed this year. From parts-per-quadrillion dioxin determinations to the determination of mercury, development work was conducted to improve our ability to analyze for a number of trace organic and metal species in drinking and surface waters. Improved quality control, lower detection limits, and more efficient extraction methods to enable LSB staff to reduce our use of toxic solvents were principal themes this year.

## I. PAH Storage Study

Study Leaders: P. Crozier

Study Team: J. Yang, L. Gurprasad, L. Matchuk

### *Introduction and Objectives*

Polynuclear aromatic hydrocarbons (PAH) are ubiquitous environmental pollutants. The carcinogenic nature of some PAHs has resulted in regulatory action. The Ontario Ministry of Environment and Energy has established the maximum acceptable concentration of benzo[a]pyrene in drinking water to be 10 ng/L.

Several researchers have noted that the presence of chlorine in drinking water samples reduces the concentration of B[a]P in some samples. It was the objective of this research to

determine an effective means of preserving concentrations of PAH, especially B[a]P, in drinking water samples that contain chlorine.

### *Results*

A variety of storage techniques for PAHs involving preservatives such as formaldehyde, ascorbic acid, and pH adjustment have been documented. The U.S. EPA laboratories use sodium thiosulphate to preserve wastewater samples. Experiments were designed to determine the extent of losses of 13 individual PAHs as well as test possible preservatives. Sodium thiosulphate and sodium sulphite were tested in this study.

PAH concentrations in distilled water reference samples remained relatively constant for the duration of the two-month study. The concentrations of B[a]P and 7,12-dimethylbenz[a]anthracene decreased significantly in chlorinated tap water samples during storage, while other PAHs were affected to a lesser extent. Super chlorination of water caused an immediate decrease in the concentrations of nine of the thirteen PAHs tested, and their virtual disappearance over the course of the study. Sodium thiosulphate effectively retarded PAH losses in all cases while sodium sulphite had little effect. The Laboratory Services Branch has now adopted the use of sodium thiosulphate as a standard preservative to be used for the determination of PAH in chlorinated water samples.

### *Work to be Completed*

Speculation concerning the mechanism of PAH loss during water chlorination include the production of chlorinated PAHs or chemical breakdown of PAHs. A recent paper has also suggested that the presence of chlorine quenches the fluorescence of PAH so they may not be detected during HPLC/fluorescence detector analysis. Mass spectrometry investigations in this study revealed the presence of small amounts of the original PAH, but no other compounds. Investigations of the fate of the PAHs in chlorinated water samples are continuing.

*Publications and Presentations*

1. P. Crozier, D. Hall, L. Gurprasad, L. Matchuk, J. Yang. *Stability of Polynuclear Aromatic Hydrocarbons in Chlorinated Drinking Water Samples*, presented at the Technology Transfer Conference, Toronto, Ontario, November 1992.
2. P. Crozier. *Polynuclear Aromatic Hydrocarbon Storage Study - November 1991 to January 1992*, Laboratory Services Branch, Drinking Water Organics Section Internal Report, 1992.

**II. Disinfection By-Products**

Study Leader: O.W. Berg

Study Team: W. Offenbacher, R. Salemi, P. Riley, J. Fracassi

*Introduction and Objectives*

Chlorine is a widely used disinfectant in drinking water treatment plants. Chlorine is also highly reactive and combines rapidly with naturally-occurring organic material (such as humic materials) to produce undesirable chlorinated organic compounds. The principal chlorination by-products are chloroform, trihalomethanes (THMs), and chlorinated aliphatic acids (especially dichloroacetic acid [DCA] and trichloroacetic acid [TCA]). The majority of disinfection by-products are non-volatile polar compounds for which ppb analysis methods do not exist.

Some of these polar compounds are halo-acetic acids and halo-acetonitriles. Their determination is important because many of these compounds are suspected carcinogens. The objectives of this research are to develop the methods needed to perform routine determination of polar organic disinfection by-products such as halo-acetic acids and halo-acetonitriles in drinking water at ppb concentrations.

### *Results*

This research is in the early stages of development. Literature searches have been completed and the process of testing various extraction methods will be underway in early 1993. The emphasis will be on micro-extraction methods and solid-phase extraction techniques, including Empore disks, resin cartridges, and ion exchange cartridges.

### *Work to be Completed*

In addition to development of the wet chemistry (extraction, sample preparation), various instrumental detection systems will be evaluated. Emphasis will be on GC-quadrupole mass spectrometry and GC-ion trap detection.

## **III. Micro-Extraction Methods for Drinking Water**

Study Leader: O.W. Berg, P. Crozier  
Study Team: W. Offenbacher

### *Introduction and Objectives*

Micro-extraction involves the manipulation of extraction conditions in such a manner that analytes can be extracted from water with a minimum amount of organic solvent. Implementation of micro-extraction methods will permit increased sample productivity and reduced analytical costs. Reduced use of solvents is beneficial from both an environmental and health & safety perspective. It is also possible that micro-extraction methods may lead to improved analytical quality by allowing reduced sample extract handling. The objective of this research is to develop, validate, and implement micro-extraction methods in the Drinking Water Analyses Section.

### *Results*

The first routine analytical micro-extraction method to be developed is for the determination of chlorinated organic pesticides and PCBs. Similar techniques have been applied to several pesticides and PCBs by the U.S. EPA (Method 505). However, the list of compounds covered by Method 505 is limited and the detection limits are much greater than those required for MOEE monitoring programs. Expanding the list of analytes monitored and reducing their detection limits are important goals of this work.

The micro-extraction method reduces the time for wet chemical sample preparation by 75% and eliminates the need for large quantities of extraction solvents. Dichloromethane use is virtually eliminated with these extraction methods. Distribution curves and equilibrium times have been established for each target analyte. Analyte recoveries have been tested at spike levels ranging from parts-per-billion to parts-per-quadrillion. Average recoveries of the 37 individual chlorinated organic pesticides, chlorinated organic industrial chemicals, and PCBs tested exceeded 85%. Relative standard deviations were in the order of 3-15%.

### *Work to be Completed*

Work on the actual method logistics is complete. The R&D report and method documentation are in preparation. Remaining experimental work includes testing of the method on a wide variety of real-matrix spiked samples and intercomparison of the micro-extraction method with the standard dichloromethane extraction method using duplicate samples. The method comparison study is important to determine whether any statistically significant differences between the two methods exist which may affect the interpretation of historical data bases.

#### **IV. Automated Determination of Mercury at Ultra-Trace Concentrations in Waters by Gold Amalgam Preconcentration and Cold-Vapour Atomic Fluorescence Spectrometry**

Study Leader: C. Chan

Study Team: R. Sadana

##### *Introduction and Objectives*

To develop a more sensitive method for the determination of mercury in waters required by the Biomaterials/Flameless AA Unit.

##### *Results*

In the method that has been developed, mercury in water samples is oxidized to its divalent ion form by an acid digestion procedure. The mercury is then reduced to its elemental form by a stannous chloride solution in a continuous flow system. The mercury vapour is diverted into a gold wire absorber via a flow injection valve to form an amalgam. Mercury is thermally desorbed and swept with argon into an atomic fluorescence spectrometer where fluorescence is measured. The detection limit of mercury using this method is 2 ng/L.

##### *Work to be Completed*

A publication describing the new method has been submitted to *Analytica Chimica Acta*.

## V. Detection of Sulphur Compounds by Ion Chromatography

Study Leader: F. Lo  
Study Team: B. Wright

### *Introduction and Objectives*

To support the studies of Water Resources Branch staff, improved methodology was needed for the determination of sulphur compounds. In the proposed method, sulphur compounds are oxidized to sulphate and detected by ion chromatography. A specific objective of the new method is to determine the optimum concentration of hydrogen peroxide for use in the oxidation step.

### *Results*

A continuous flow system for mixing the sample with hydrogen peroxide was constructed. The oxidation product of the sulphur compounds was shown to be sulphate. Satisfactory separation of sulphate from other ions in the sample was achieved by using a Dionex anion separator column. The new method was applied to the analysis of Dorset water samples.

### *Work to be Completed*

The completeness of the oxidation step must be determined, and the new method validated. A report on this work is in preparation.



## VI. Mercury Determination by ICP-MS

Study Leader: M. Powell  
Study Team: E. Quan, D. Wiederin

### *Introduction and Objectives*

Direct Injection Nebulization (DIN) is a new sample introduction system for Inductively Coupled Plasma (ICP) that increases efficiency of sample transport to the plasma. Use of this technology will result in a more efficient use of complex, expensive ICP-MS instrumentation and faster sample turnaround for our clients. The new methodology could save 1.5 staff-years in sample preparation time and result in improved quality control, faster sample turnaround, and lower cost.

### *Results*

A feasibility study using a crude "home-built" apparatus was completed. Results showed that application of the DIN device to the determination of trace metals in drinking water should enhance detection limits and sample throughput. By using the DIN, mercury could be included in the same scan now used to determine other metals in drinking water by ICP-MS. This saves the need for a separate analysis for only mercury.

During the course of this work a commercial DIN developed by Cetac Technologies, Nebraska, was evaluated. In addition to exhibiting excellent performance, the commercial device is automated, and can incorporate the use of ion chromatography columns to allow chromatographic separation of analytes prior to ICP-MS detection. This will permit additional application of the DIN-ICP-MS system to metal speciation studies and to the determination of organometallics.

### *Work to be Completed*

The original feasibility study is nearing completion for multi-element determinations. Additional investigations are underway to apply the DIN-ICP-MS system to the determination of organometallics.

### *Publications and Presentations*

1. M.J. Powell, E.S.K. Quan, D.W. Boomer, and D. Wiederin. *An Improved Technique for Mercury Analysis of Drinking Water Using Direct Injection Nebulization and ICP-MS*; presented at the 38th Canadian Spectroscopy Conference, Trent University, Peterborough, Ontario, August 1992.
2. M.J. Powell, E.S.K. Quan, D.R. Wiederin, D.W. Boomer. *Inductively Coupled Plasma Mass Spectrometry with Direct Injection Nebulization for Mercury Analysis of Drinking Water*, Anal. Chem. **1992**, 64, 2253-7.

## **VII. Improved Extraction Methods for PCDDs and PCDFs in Aqueous Samples**

Study Leader: K. Taylor

Study Team: L. Grey, K. Taylor, V. Khurana

### *Introduction and Objectives*

Extraction of aqueous samples is typically done by liquid/liquid extraction which requires a considerable amount of solvent. Groundwater samples are filtered to separate the particulate and aqueous portions. The particulate portion is solid/liquid extracted using a Soxhlet extractor, while the aqueous portion is liquid/liquid extracted. By using solid phase extraction, a considerable saving in solvent use can be realized. In addition, faster sample throughput and improved quality control (because of reduced sample handling) are possible.

### *Results*

The Dioxin/Furan Unit is examining the use of Empore disks for the extraction efficiency of dioxins and furans from 2L water samples. To date, the 90 mm disks have been successfully used for the extraction of pulp and paper samples. Samples with up to 15% particulate load were

rapidly extracted, within 30 minutes, using Whatman glass fibre filters in series with the empore disk. The PCDDs and PCDFs adsorbed on particulates are trapped on the glass fibre filter while the dissolved PCDDs and PCDFs are adsorbed by the Empore disk. The glass fibre filter paper and Empore disk are then extracted together in the Soxhlet apparatus. This eliminates the liquid/liquid extraction step and the use of methylene chloride (a chlorinated solvent) from the method. Method recoveries, ranging from 80 to 110%, compare favourably with results of the current liquid/liquid extractions.

#### *Work to be Completed*

Due to the exceptional efficiency of the 90 mm disks with pulp and paper samples, future investigations will explore the more cost effective 47 mm disks for the extraction of sample with little or no particulate loadings such as cooling or drinking waters. Breakthrough studies will be completed and further experimental work will be based on these results. This technology looks very promising for groundwater, wastewater, drinking water and MISA samples. It is expected that the solid phase extraction method will eliminate the use of dichloromethane for extraction of aqueous samples and at the same time improve extraction efficiency and reduce extraction time.

### **VIII. Analysis of Sewage Sludge for Organic, Extractable Priority Pollutants**

Study Leader: R. Lega

Study Team: J. Ladwig, O. Meresz

#### *Introduction and Objectives*

The increasing concern about water pollution and hazardous waste control has raised interest in the fate of a wide range of organic contaminants during the waste water treatment process. The sewage sludge produced contains many contaminants, including organic compounds adsorbed onto the sludge solids. The objective of this research was to develop and validate an analytical procedure for the determination of extractable organic priority pollutants (phenolics,

phenoxy acids, base/neutrals, PCBs, chloroaromatics, organochlorine pesticides) in municipal sewage sludge.

### *Results*

The development work reported in last year's annual report was refined and completed. The extraction procedure employs sample homogenization, centrifugation for particulate removal, pH adjustment, and extraction using a mixture of diethylether and dichloromethane (2:1 v/v). Samples were cleaned-up by an automated procedure using gel permeation chromatography, and Target compounds were determined by GC/MS. Recoveries, method detection limits, and other quality control data for target compounds were determined. Method documentation was completed, and some real sample analyses were successfully carried out.

### *Work to be Completed*

The method is essentially complete. However, better performance for a few target analytes is desired (phenols and alkyl phenols).

### *Publications and Presentations*

1. R. Lega, J. Ladwig, O. Meresz, G. Crawford, D. Toner, Y. Jones, and I. Ahmad. *Analysis of Sewage Sludge for 100 Organic Priority Pollutants at Part per Billion Levels*, presented at the Technology Transfer Conference, Toronto, Ontario, November 1992.

# Multi-Program Support

## Introduction

Many analytical methods support a number of programs and Branches. For example, R&D work to improve the precision of gas chromatography-mass spectrometry determinations will benefit all LSB clients who submit samples for the determination of organic pollutants. Sometimes these projects are started because of a specific client request (i.e. to reach lower detection levels), but often such studies are initiated by LSB staff as an ongoing effort to improve analytical capability and to bring on-line new technologies that will benefit our clients by providing faster turnaround, increased sample capacity, better specificity, or improved accuracy and precision.

## **I. Negative Ion Chemical Ionization (NICI) Confirmation of Halogenated Organic Compounds**

Study Leader: V. Taguchi  
Study Team: D. Robinson

### *Introduction and Objectives*

The majority of analyses done by gas chromatography/mass spectrometry (GC/MS) are performed with the mass spectrometer operated in the electron (impact) ionization (EI) mode where only positive ions are detected. This technique has been applied successfully to the analysis of a wide range of organic compounds. For halogenated organic compounds such as polychlorinated biphenyls (PCB), presently being analyzed by electron capture detection (ECD),

comparable detection limits cannot be obtained by EI. However, operation of the mass spectrometer in the NICI mode will provide comparable detection limits to ECD and additional structural information from the NI mass spectrum. Therefore, the goals of this research are to investigate NICI as a method for analyzing halogenated organic compounds and to establish a library of NICI spectra that will be used to confirm the presence of halogenated target analytes.

### *Results*

A gas manifold system has been designed and built to accommodate 3 reagent gases: methane, isobutane and CO/H<sub>2</sub>. Ammonia is also available. These reagent gases can be used for both positive and negative ion CI.

The CI experiments were set up on the 2 Finnigan 4500 mass spectrometers and these systems were optimized for NICI analyses.

Fish extracts from Thunder Bay were submitted for confirmation of toxaphene. Toxaphene is a complex mixture of polychlorinated camphenes. With pattern recognition techniques in ECD analyses, it can be difficult to distinguish toxaphene from other chlorinated terpenes and PCB's. One fish extract thought to contain toxaphene actually contained PCB's and chlorinated terpenes. The presence of toxaphene was confirmed by NICI in another extract. These results demonstrated the utility of the NICI technique for confirmational analyses.

### *Work to be Completed*

GC/MS analyses performed by EI are facilitated by the availability of libraries of standard mass spectra [e.g. National Institute of Standards and Technology (NIST), Wiley]. On the other hand, no commercial libraries of NICI spectra are available. Therefore, standards of halogenated organics are being acquired and NICI spectra are being obtained to create an in-house library of NICI spectra. Confirmational identifications for these compounds will then be available on a routine basis.

## II. LC-MS Analysis of Environmental Samples

Study Leader: V. Taguchi  
Study Team: C. Koester

### *Introduction and Objectives*

For the determination of organic pollutants in environmental samples, gas chromatography-mass spectrometry (GC-MS) is generally used. However, GC-MS is only applicable to about 20% of known organic compounds. Analytes that have high molecular weights, that are highly polar (underivatized), or that are thermally labile are difficult to determine by GC-MS. Liquid Chromatography-Mass Spectrometry (LC-MS) is an emerging technology which is capable of determining many of these substances. The goals of this project are to optimize an HP 1090 LC- VG Trio 2 MS system with particle-beam interface for the identification of unknown compounds and target analytes in environmental samples. LC-MS will complement the existing GC-MS capabilities of the mass spectrometry laboratory.

### *Results*

After evaluating three nebulizer designs, a nebulizer that works reproducibly was obtained; the relative standard deviation of the areas produced by replicate injections of a standard is 10% or less. This has permitted the estimation of instrumental detection limits for selected compounds, many of which cannot be analyzed by GC-MS. Following is a list of standards analyzed by LC-MS and the instrumental detection limits which were obtained under full scan conditions (43 - 510 amu/1 s): benzidine, 60 ng; caffeine, 20 ng; carbaryl, 40 ng; carbofuran, 200 ng; diallate, 2700 ng; dichlorobenzidine, 10 ng; diuron, 20 ng; linuron, 80 ng; monuron, 200 ng; phenanthrene, 90 ng; siduron, 70 ng; trifluralin, 230 ng. To date, the addition of buffers to the mobile phase has not improved detection limits. Selected ion monitoring is expected to improve detection limits for target analytes one hundred-fold. Sample extracts have continued to be analyzed;  $S_8$ , octadecenoic acids, phthalates, metolachlor, and atrazine have been detected by LC-MS.

*Work to be Completed*

The use of LC-MS for identifying organics not amenable to GC-MS determination will continue. Routine extraction procedures and method detection limits for selected analytes, both full scan and selected ion monitoring, will be determined. The use of different mobile phase compositions will be investigated. A manual describing LC-MS operation, troubleshooting, and quality assurance/quality control issues will be written to provide technology transfer. This project is expected to be completed in late 1993.

*Publications and Presentations*

1. C. J. Koester, R. E. March, D. T. Wang, and V. Y. Taguchi. *Analysis of Organic Compounds by Liquid Chromatography/Mass Spectrometry (LC/MS)*, presented at the Technology Transfer Conference, Toronto, Ontario, November, 1992.
2. C. J. Koester. *Analysis of Organic Compounds by Liquid Chromatography/Mass Spectrometry*, Department of Chemistry Seminar, Trent University, Peterborough, Ontario, September 1992.

### **III. Determination of As and Se in Environmental Samples by Flow-Injection Hydride Generation Atomic Absorption Spectrometry**

Study Leader: C. Chan  
Study Team: R. Sadana

*Introduction and Objectives*

To develop a more sensitive method with greater throughput for the determination of As and Se in environmental samples required by the Biomaterials/Flameless AAS Unit.



### *Results*

Flow injection is applied to sample introduction in conjunction with automated hydride generation and AAS for the determination of As and Se in environmental samples. A large sample loop was used to provide high sensitivity. The samples (except waters) are digested with a mixture of acids.  $\text{Se}^{6+}$  in the digested solutions is pre-reduced to  $\text{Se}^{4+}$  in 6-8 M HCl, and  $\text{As}^{5+}$  to  $\text{As}^{3+}$  by KI. The analyte is then converted to hydride by  $\text{NaBH}_4$ . The evolved hydride is carried through to an atomizer, and the atomic absorption signal is measured. Detection limits for both As and Se are 0.3 ng/mL, equivalent to 75 ng/g in solid samples.

### *Work to be Completed*

The project is complete. A paper describing this research was published in *Analytica Chimica Acta*.

### *Publications and Presentations*

1. C. Chan and R. Sadana. *Determination of Arsenic and Selenium in Environmental Samples by Flow Injection - Hydride Generation Atomic Absorption Spectrometry*, *Analytica Chimica Acta* **1992**, 270, 231-8.

## **IV. Extraction of Chlorophenols from Sediment by Supercritical Fluid Extraction**

Study Leader: R. Brunato  
Study Team: D. Toner

### *Introduction and Objectives*

Elimination of toxic solvents from laboratories is a difficult task, because the determination of organic pollutants in environmental samples requires the analytes to be removed

from the bulk sample matrix by liquid extraction using such solvents. One method that has shown much promise for replacing toxic solvents in such extractions is supercritical fluid extraction (SFE) by using liquid CO<sub>2</sub>. In addition to eliminating the need for the use of toxic solvents in the extraction step, SFE extractions are often more rapid and may give higher analyte recoveries for some applications. In this study, the use of SFE for chlorophenols in sediment samples was investigated.

### *Results*

A Hewlett-Packard supercritical fluid extractor (SFE) was used for this study. A major contamination problem was traced to the Medigas CO<sub>2</sub> supply employed. Some parts of the SFE extractor could not be cleaned and were replaced. A pure supply of CO<sub>2</sub> from Air Products was used for the remainder of this work.

Precision studies were conducted by analysis of replicates of spiked sand. Accurate and reproducible results were achieved for spikes after several operational improvements suggested by B. Lee (Canada Centre for Inland Waters) were implemented. Validation studies by analysis of replicate spiked samples and by analysis of a chlorophenol Certified Reference Material (Fisher Scientific) were then completed. Validation included parallel extractions of real samples (SFE vs Soxhlet extraction).

### *Work to be Completed*

All work has been completed for this project, and the method documentation has been prepared.

## Publications and Presentations - 1992

### Laboratory Services Branch

#### A. Publications

1. P. Crozier. *Polynuclear Aromatic Hydrocarbon Storage Study - November 1991 to January 1992*, Laboratory Services Branch, Drinking Water Organics Section Internal Report, 1992.
2. M.J. Powell, E.S.K. Quan, D.R. Wiederin, D.W. Boomer. *Inductively Coupled Plasma Mass Spectrometry with Direct Injection Nebulization for Mercury Analysis of Drinking Water*, Anal. Chem. **1992**, 64, 2253-7.
3. C. Chan and R. Sadana. *Determination of Arsenic and Selenium in Environmental Samples by Flow Injection - Hydride Generation Atomic Absorption Spectrometry*, *Analytica Chimica Acta* **1992**, 270, 231-8.
4. C. Tashiro, R.E. Clement, P. Steer, C. Chiu, and T. Dann. *State-of-the-Art Capability for Determination of Chlorinated Dioxins and Dibenzofurans in Ambient Air*; Proceedings of the EPA/AWMA Symposium *Measurement of Toxic and Related Air Pollutants*, in press.
5. V.Y. Taguchi, D.T. Wang, S.W.D. Jenkins, R.J. Kleins and R.E. Clement. *A Classification System for the Identification of Organics by Gas Chromatography/Mass Spectrometry*; *Canadian Journal of Applied Spectroscopy*, **1992**, 37(5), 145-148.
6. G.A. Eiceman, R.E. Clement, and H.H. Hill, Jr. *Gas Chromatography*; *Analytical Chemistry*, **1992**, 64, 170R-180R.

7. R.E. Clement. *Sampling for Environmental Analysis: A Classroom Experiment You Can Sink Your Teeth Into!*, *Analytical Chemistry*, **1992**, 64, 1076A-1081A.
8. R.E. Clement and E.J. Reiner. *Mass Spectrometry Detectors*, in *Detectors for Capillary Chromatography*; H.H. Hill and D.G. McMinn, editors; John Wiley & Sons, **1992**, chapter 13, pp 327-53.
9. R.E. Clement, C. Tashiro, E.J. Reiner, P. Steer, M. Lusi, T. Dann. *Comparison of High and Low Resolution Mass Spectrometer Performance in an Ambient Air Round Robin Study*, in *Organohalogen Compounds*, **1992**, Volume 8, pp 31-4.
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11. S. Green, P. Campbell, P. Wilson, J. McBride. *Preliminary Investigation of Phenolic Contamination of Samples by Field Autosamplers*, Environment Ontario, Laboratory Services Branch Report (ISBN 0-77780-077-2), June 1992.
12. D.E. King. *Misuse of the Null Hypothesis in Data Reporting and Interpretation*, Environment Ontario, Laboratory Services Branch Report, October 1992.
13. D.E. King. *Determination of Mercury in Fish Tissue. Part I: Performance Criteria*, Environment Ontario, Laboratory Services Branch Report, October 1992.
14. M.J. Powell, E.S.K. Quan, D.W. Boomer, D. Wiederin. *An Improved Technique for Mercury Analysis of Drinking Water Using Direct Injection Nebulization and ICP-MS*; presented at the 38th Canadian Spectroscopy Conference, Trent University, Peterborough, Ontario, August 1992.
15. B.P. Bourgoin, D. Boomer, M.J. Powell, S. Willie, D. Edgar, D. Evans. *Instrumental Comparison for the Determination of Cadmium and Lead in Calcium Supplements and Other Calcium-rich Matrices*, *Analyst*, **1992**, 117, 19-22.

16. M.B. Campbell and G.A. Kanert. *High-pressure Microwave Digestion for the Determination of Arsenic, Antimony, Selenium and Mercury in Oily Wastes, Analyst, 1992*, 117, 121-124.
17. E. Duchoslav, editor. *1991 Performance Report: Drinking Water Organics Section*, Ontario Ministry of the Environment, Laboratory Services Branch Report, April 1992.
18. S. Selliah. *An Automated Graphical Procedure for Rapid Evaluation of Interlaboratory Studies*, Ontario Ministry of the Environment, Laboratory Services Branch Report (ISBN 0-7729-9894-9), May 1992.
19. R.E. Clement, editor. *Determination of Chlorinated Dibenzo-p-dioxins and Chlorinated Dibenzofurans in Ambient Air*; proceedings of a workshop held September 17, 1989, Toronto Ontario; published October, 1992.
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21. S. Cussion. *Interlaboratory Study 90-5: Volatile Organics (MISA Test Groups 17 & 18) in Reagent Water*, Ontario Ministry of the Environment, Laboratory Services Branch Report (ISBN 0-7729-9401-2), February 1992.
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#### B. Presentations

1. P. Crozier, D. Hall, L. Gurprasad, L. Matchuk, J. Yang. *Stability of Polynuclear Aromatic Hydrocarbons in Chlorinated Drinking Water Samples*, presented at the *Technology Transfer Conference*, Toronto, Ontario, November 1992.
2. E.J. Reiner. *Analyzing Samples for Dioxins*, presented at the Government of Ontario Analytical Laboratory System Annual Conference, Toronto, Ontario, September 22, 1992.
3. C. J. Koester, R. E. March, D. T. Wang, and V. Y. Taguchi. *Analysis of Organic Compounds by Liquid Chromatography/Mass Spectrometry (LC/MS)*, presented at the *Technology Transfer Conference*, Toronto, Ontario, November, 1992.

4. C. J. Koester. *Analysis of Organic Compounds by Liquid Chromatography/Mass Spectrometry*, Department of Chemistry Seminar, Trent University, Peterborough, Ontario, September 1992.
5. E.J. Reiner, R.E. Clement, C. Tashiro, P. Steer, M. Lusi, T. Dann. *Comparison of Mass Spectrometer Performance in an Ambient Air Round-Robin Study*, poster presented at the International Symposium on Chlorinated Dioxins and Related Compounds (Dioxin '92), Tampere, Finland, August 24-28, 1992.
6. K.A. McPherson, A. Johnson, A. Hayton, T. Kolic, K. Taylor, E.J. Reiner. *Characteristic Levels of Chlorinated Dibenzo-p-dioxins and Chlorinated Dibenzofurans in Ontario Lakes*, presented at the Technology Transfer Conference, Ontario Ministry of the Environment, Toronto, Ontario, November 1992.
7. R.E. Clement. *Needle in a Haystack: the Analysis of Air, Water, Soil, and Biota for Dioxin*, McBryde Medal Address presented at the 75th Canadian Chemical Conference, Edmonton, Alberta, June 1, 1992.
8. R.E. Clement and D. Boomer. *Technology Transfer for Environmental Analysis: Keeping up with the Joneses*, invited talk presented at the Canadian Spectroscopy Conference, Peterborough, Ontario, August 10-12, 1992.
9. R.E. Clement. *Dioxin and Food*, presented at the Government of Ontario Analytical Laboratory System Annual Conference, Toronto, Ontario, September 22, 1992.
10. R.E. Clement. *How We Study Dioxins in the Environment*, invited talk presented at the Science Teachers' Association of Ontario conference, Toronto, Ontario, November 5, 1992.
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12. R.E. Clement. *The MOE Dioxin Laboratory*, invited talk presented at the American Water Works Association conference, Toronto, Ontario, November 18, 1992.

13. P. Crozier and D. Hall. *Application of a Multidimensional Chromatographic/Mass Spectrometric Detection System to Trace Level Pesticides Analysis*, presented at the Technology Transfer Conference, Toronto, Ontario, November 1992.
14. M. Charbonneau, W. Craig, B. Knight, R. Walker, P. Crozier, D. Hall. *Thermal Desorption of Solid Phase Extraction Columns for the Low Level Measurement of Organic Compounds in Water*, presented at the Technology Transfer Conference, Toronto, Ontario, November 1992.





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